Claims

What is claimed is:

- 1. Use of an oxidopyrylium species as an intermediate in a chemical reaction, wherein the oxidopyrylium species is generated photochemically.
- 2. The use as in claim 1, wherein the oxidopyrylium species is generated via a process comprising an excited state intramolecular proton transfer.
- 3. The use as in claim 2, wherein the oxidopyrylium species is photochemically generated from a 3-hydroxychromone derivative with the following chemical structure:

wherein R₁, R₂, R₃, R₄ and R are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

4. The use as in claim 2, wherein the oxidopyrylium species is photochemically generated from a 3-hydroxyflavone derivative with the following chemical structure:

$$R_{2}$$
 R_{1}
 O
 OH
 R_{9}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈ and R₉ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroary 1.

5. The use as in claim 4, wherein the 3-hydroxyfla vone derivative has one of the following chemical structures:

6. The use as in claim 2, wherein the oxidopyrylium species is photochemically generated from a 5-hydroxy-2,3-dihydropyram-4-one derivative with the following chemical structure:

$$R_1$$
 O O R_2 R_3 O R R_4 $(IIII)$

wherein R₁, R₂, R₃, R₄ and R are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy,

heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

- 7. The use as in claim 2, wherein the chemical reaction comprises a cycloaddition leading to the formation of an adduct.
- 8. The use as in claim 7, wherein the cycloaddition comprises a 1,3-dipolar cycloaddition.
- 9. The use as in claim 7, wherein the chemical reaction further comprises converting the adduct formed.
- 10. A method comprising steps of:

 photochemically generating an oxidopyrylium species from a 3hydroxychromone derivative; and
 reacting the oxidopyrylium species with a dipolarophile.
- 11. The method of claim 10, wherein the oxidopyrylium species is photochemically generated *via* a process comprising an excited state intramolecular proton transfer.
- 12. The method of claim 11, wherein the oxidopyrylium species is photochemically generated from a 3-hydroxychromone derivative with the following chemical structure:

$$\begin{array}{c|c}
R_2 & R_1 & O \\
R_3 & R_4 & O \\
\hline
 & & & & \\
\hline
 & & & \\
\hline
 & & & & \\
\hline
 &$$

wherein R₁, R₂, R₃, R₄ and R are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)C(=O)N(R_x)₂, -N(R_x)C(=O)N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

13. The method of claim 12, wherein the oxidopyrylium species is photochemically generated from a 3-hydroxyflavone derivative with the following chemical structure:

$$R_2$$
 R_3
 R_4
 R_5
 R_6
 R_7
 R_6

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈ and R₉ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CFH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -

OC(=O) R_x , -OCO₂ R_x , -S(O) R_x , -S(O)₂ R_x , -NR_x(CO) R_x , -N(R_x)CO₂ R_x , -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂ R_x , and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

14. The method of claim 13, wherein the 3-hydroxyflavone derivative has one of the following chemical structures:

- 15. The method of claim 11, wherein the reaction between the oxidopyrylium species and the dipolarophile comprises a cycloaddition leading to the formation of an adduct.
- 16. The method of claim 15, wherein the cycloaddition comprises a 1,3-dipolar cycloaddition.
- 17. The method of claim 15, wherein the dipolar ophile is a cinnamate derivative.
- 18. The method of claim 15 further comprising converting the adduct formed
- 19. The method of claim 18, wherein the adduct formed comprises an aglain core structure and wherein converting the adduct formed results in formation of a ring system selected from the group consisting of an aglain ring system, a rocaglamide ring system, and a forbaglin ring system.
- 20. A method for preparing a compound with an aglain core structure, the method comprising steps of:
 - producing an oxidopyrylium species (I_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxychromone derivative (I); and

reacting the oxidopyrylium species with a dipolar ophile (IV) to obtain the aglain core-containing compound (V), wherein compounds (I), (I_T), (IV) and (V) have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)C(=O)N(R_x)₂, -N(R_x)C(-O)N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

21. A method for preparing a compound with an aglain core structure, the method comprising steps of:

producing an oxidopyrylium species (Π_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxyflavone derivative (Π); and reacting the oxidopyrylium species with a dipolarophile (Π) to obtain the aglain core-containing compound (Π), wherein compounds (Π), (Π_T), (Π) and (Π) have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHC1₂, -CH₂OH, -CH₂CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

22. The method of claim 21, wherein the 3-hydroxyflavone derivative has one of the following chemical structures:

23. The method of claim 20 or 21, wherein the dipolarophile (IV) is a cinnamate derivative with the following chemical structure:

$$R^{1}$$

$$R^{2}$$

$$R^{3}$$

$$R^{6}$$

$$R^{5}$$

wherein R¹ is selected from the group consisting of hydrogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, and a protecting group; and

wherein R², R³, R⁴, R⁵, and R⁶ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R'_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

- 24. The method of claim 20 or 21 further comprising converting the aglain corecontaining compound.
- 25. The method of claim 24, wherein converting the aglain core-containing compound results in formation of a compound with a ring system selected from the group consisting of an aglain ring system, a rocaglamide ring system, and a forbaglin ring system.
- 26. The method of claim 25, wherein converting the aglain core-containing compound into a compound with an aglain ring system comprises a reduction.

27. The method of claim 25, wherein converting the aglain core-containing compound into a compound with a rocaglamide ring system comprises an α-ketol (acyloin) rearrangement and, optionally, a hydroxyl-directed reduction.

- 28. The method of claim 27, wherein the α -ketol (acyloin) rearrangement comprises a base-mediated reaction.
- 29. The method of claim 25, wherein converting the aglain core-containing compound into a compound with a forbaglin ring system comprises an oxidative cleavage.
- 30. A method for preparing an aglain derivative, the method comprising steps of: producing an oxidopyrylium species (I_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxychromone derivative (I); reacting the oxidopyrylium species with a dipolarophile (IV) to obtain a compound with an aglain core structure (V); and converting the compound with an aglain core structure into an aglain

converting the compound with an aglain core structure into an aglain derivative (VI), wherein compounds (I), (I_T), (IV), (V) and (VI) have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl,

alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl; and

wherein R' is selected from the group consisting of hydrogen, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -S(O)R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, and -N(R_x)S(O)₂R_x,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

31. A method for preparing an aglain derivative, the method comprising steps of: producing an oxidopyrylium species (II_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxyflavone derivative (II);

reacting the oxidopyrylium species with a dipolarophile (IV) to obtain a compound with an aglain core structure (V'); and

converting the compound with an aglain core structure into an aglain derivative (VI'), wherein compounds (II), (II_T), (IV), (V') and (VI') have the following chemical structures:

$$R_{2}$$
 R_{1}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{7}
 R_{1}
 R_{2}
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{7}
 R_{8}
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{7}
 R_{8}
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{7}
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{7}
 R_{7}

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHC1₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl; and

wherein R' is selected from the group consisting of hydrogen, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, $-CH_2OH$, $-CH_2CH_2OH$, $-CH_2SO_2CH_3$, $-C(=O)R_x$, $-CO_2(R_x)$, $-C(=O)N(R_x)_2$, $-S(O)R_x$, $-NR_x(CO)R_x$, $-N(R_x)CO_2R_x$, $-N(R_x)C(=O)N(R_x)_2$, and $-N(R_x)S(O)_2R_x$,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

32. The method of claim 31, wherein the 3-hydroxyflavone derivative has one of the following chemical structures:

33. The method of claim 30 or 31, wherein the dipolarophile (IV) is a cinnamate derivative with the following chemical structure:

$$R^{1}$$
 R^{2}
 R^{3}
 R^{6}
 R^{5}

wherein R¹ is selected from the group consisting of hydrogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, and a protecting group; and

wherein R², R³, R⁴, R⁵, and R⁶ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

34. The method of claim 30 or 31, wherein converting the compound with an aglain core structure into an aglain derivative comprises a reduction.

35. The method of claim 34, wherein the reduction comprises using NaBH₄ or Me₄BH(OAc)₃.

- 36. The method of claim 30 or 31, wherein converting the compound with an aglain core structure into an aglain derivative comprises addition of a nucleophile.
- 37. A method for preparing a rocaglamide derivative, the method comprising steps of:

producing an oxidopyrylium species (I_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxychromone derivative (I);

reacting the oxidopyrylium species obtained with a dipolarophile (IV) to obtain a compound with an aglain core structure (V); and

converting the compound with an aglain core structure into a rocaglamide derivative (VII), wherein compounds (I), (I_T), (IV), (V), and (VII) have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x,

 $-S(O)R_{x_0}$ $-S(O)_2R_{x_0}$ $-NR_x(CO)R_{x_0}$ $-N(R_x)CO_2R_{x_0}$ $-N(R_x)C(=O)N(R_x)_2$, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

38. A method for preparing a rocaglamide derivative, the method comprising steps of:

producing an oxidopyrylium species (Π_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxyflavone derivative (Π) ;

reacting the oxidopyrylium species obtained with a dipolarophile (IV) to obtain a compound with an aglain core structure (V'); and

converting the compound with an aglain core structure into a rocaglamide derivative (VII'), wherein compounds (II), (III), (IV), (V'), and (VII') have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHC1₂, -CH₂OH, -CH₂CH₂OH, -

CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

39. The method of claim 38, wherein the 3-hydroxyflavone derivative has one of the following chemical structures:

40. The method of claim 37 or 38, wherein the dipolarophile (IV) is a cinnamate derivative with the following chemical structure:

$$R^{1} \qquad R^{2} \qquad R^{3}$$

$$R^{6} \qquad R^{5}$$

wherein R¹ is selected from the group consisting of hydrogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, and a protecting group; and

wherein R², R³, R⁴, R⁵, and R⁶ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x,

 $-S(O)R_x$, $-S(O)_2R_x$, $-NR_x(CO)R_x$, $-N(R_x)CO_2R_x$, $-N(R_x)C(=O)N(R_x)_2$, $-N(R_x)S(O)_2R_x$, and $-S(O)_2N(R_x)_2$,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

- 41. The method of claim 37 or 38, wherein converting the compound with an aglain core structure into a rocaglamide derivative comprises an α-ketol (acyloin) rearrangement and, optionally, a hydroxyl-directed reduction.
- 42. The method of claim 41, wherein the α-ketol (acyloin) rearrangement comprises a base-mediated reaction.
- 43. A method for preparing a rocaglamide derivative, the method comprising steps of:

producing an oxidopyrylium species (I_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxychromone derivative (\mathbf{I}) ;

reacting the oxidopyrylium species obtained with a dipolarophile (IV) to obtain a compound with an aglain core structure (V); and

converting the compound with an aglain core structure into a rocaglamide derivative (VIII), wherein compounds (I), (I_T), (IV), (V), and (VIII) have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy,

heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl; and

wherein R' is selected from the group consisting of hydrogen, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, $-CH_2OH$, $-CH_2CH_2OH$, $-CH_2SO_2CH_3$, $-C(=O)R_x$, $-CO_2(R_x)$, $-C(=O)N(R_x)_2$, $-S(O)R_x$, $-NR_x(CO)R_x$, $-N(R_x)CO_2R_x$, $-N(R_x)C(=O)N(R_x)_2$, and $-N(R_x)S(O)_2R_x$,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

- 44. A method for preparing a rocaglamide derivative, the method comprising steps of:
 - producing an oxidopyrylium species (\mathbf{H}_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxyflavone derivative (\mathbf{H}) ;
 - reacting the oxidopyrylium species obtained with a dipolar ophile (ΓV) to obtain a compound with an aglain core structure (V'); and
 - converting the compound with an aglain core structure into a rocaglamide derivative (VIII'), wherein compounds (II), (II_T), (IV), (V'), and (VIII') have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHC1₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl; and

wherein R' is selected from the group consisting of hydrogen, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -CH₂OH, -CH₂CH₂OH, -CH₂CO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -S(O)R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, and -N(R_x)S(O)₂R_x,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

45. The method of claim 44, wherein the 3-hydroxyflavone derivative has one of the following chemical structures:

46. The method of claim 43 or 44, wherein the dipolar ophile (IV) is a cinnamate derivative with the following chemical structure:

$$R^{1}$$
 R^{2}
 R^{3}
 R^{6}
 R^{5}

wherein R¹ is selected from the group consisting of hydrogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, and a protecting group; and

wherein R², R³, R⁴, R⁵, and R⁶ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -N(R_x)CO₂R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

- 47. The method of claim 43 or 44, wherein converting the compound with an aglain core structure into a rocaglamide derivative comprises an α-ketol (acyloin) rearrangement and, optionally, a hydroxyl-directed reduction.
- 48. The method of claim 47, wherein the α-ketol (acyloin) rearrangement comprises a base-mediated reaction.
- 49. A method for preparing a forbaglin derivative, the method comprising steps of:

producing an oxidopyrylium species (I_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxychromone derivative (I);

reacting the oxidopyrylium species obtained with a dipolarophile (IV) to obtain a compound with an aglain core structure (V); and

converting the compound with an aglain core into a forbaglin derivative (IX), wherein compounds (I), (I_T), (IV), (V) and (IX) have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R, R", R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl,

alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -CN₁, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OCO₂R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroary L.

50. A method for preparing a forbaglin derivative, the method comprising steps of:

producing an oxidopyrylium species (Π_T) by photoinduced excited state intramolecular proton transfer of a 3-hydroxy: flavone derivative (Π) ;

reacting the oxidopyrylium species obtained with a dipolarophile (IV) to obtain a compound with an aglain core structure (V'); and

converting the compound with an aglain core into a forbaglin derivative (IX'), wherein compounds (II), (II_T), (IV), (V') and (IX') have the following chemical structures:

wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R', R_a and R_b are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroalkoxy, thioalkyl, thioaryl,

acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, $-NO_2$, -CN, $-CF_3$, $-CH_2CF_3$, $-CHC1_2$, $-CH_2OH$, $-CH_2CH_2OH$, $-CH_2SO_2CH_3$, $-C(=O)R_x$, $-CO_2(R_x)$, $-C(=O)N(R_x)_2$, $-OC(=O)N(R_x)_2$, $-OC(=O)R_x$, $-OCO_2R_x$, $-S(O)R_x$, $-S(O)_2R_x$, $-NR_x(CO)R_x$, $-N(R_x)CO_2R_x$, $-N(R_x)C(=O)N(R_x)_2$, $-N(R_x)S(O)_2R_x$, and $-S(O)_2N(R_x)_2$,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

51. The method of claim 50, wherein the 3-hydroxyflavone derivative has one of the following chemical structures:

52. The method of claim 49 or 50, wherein the dipolarophile (IV) is a cinnamate derivative with the following chemical structure:

$$R^{1}$$

$$R^{2}$$

$$R^{3}$$

$$R^{6}$$

$$R^{5}$$

wherein R^I is selected from the group consisting of hydrogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, and a protecting group; and

wherein R², R³, R⁴, R⁵, and R⁶ are identical or different and selected from the group consisting of hydrogen, halogen, hydroxy, alkoxy, aryloxy, heteroalkoxy, heteroaryloxy, thioalkyl, thioaryl, acyl, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, heteroaryl, alkylamino, amino alkyl, arylamino, amino aryl, a protecting group, -NO₂, -

CN, -CF₃, -CH₂CF₃, -CHCl₂, -CH₂OH, -CH₂CH₂OH, -CH₂SO₂CH₃, -C(=O)R_x, -CO₂(R_x), -C(=O)N(R_x)₂, -OC(=O)N(R_x)₂, -OC(=O)R_x, -OC(=O)R_x, -OCO₂R_x, -S(O)R_x, -S(O)₂R_x, -NR_x(CO)R_x, -N(R_x)CO₂R_x, -N(R_x)C(=O)N(R_x)₂, -N(R_x)S(O)₂R_x, and -S(O)₂N(R_x)₂,

wherein each occurrence of R_x is independently selected from the group consisting of hydrogen, aliphatic, alicyclic, heteroaliphatic, heterocyclic, aromatic, heteroaromatic, aryl, and heteroaryl.

- 53. The method of claim 49 or 50, wherein converting the compound with an aglain core structure into a forbaglin derivative comprises an oxidative cleavage.
- 54. The method of claim 53, wherein the oxidative cleavage comprises using Pb(OAc)₄.
- A compound with an aglain core structure prepared by the method of claim 20, wherein the aglain-core containing compound has the following chemical structure:

$$R_{2}$$
 R_{3}
 R_{4}
 R_{4}
 R_{4}
 R_{5}
 R_{6}
 R_{1}
 R_{2}
 R_{4}
 R_{4}
 R_{5}
 R_{5}

A compound comprising an aglain core structure prepared by the method of claim 21, wherein the aglain-core containing compound has the following chemical structure:

$$R_{2}$$
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{7}
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}

57. An aglain derivative prepared by the method of claim 30, wherein the aglain derivative has the following chemical structure:

$$R_2$$
 R_3
 R_4
 R_4
 R_5
 R_4
 R_5
 R_6
 R_7
 R_8
 R_8
 R_8
 R_8
 R_8
 R_8

An aglain derivative prepared by the method of claim 31, wherein the aglain derivative has the following chemical structure:

59. A rocaglamide derivative prepared by the method of claim 37, wherein the rocaglamide derivative has the following chemical structure:

$$R_{2}$$
 R_{3}
 R_{4}
 R_{4}
 R_{1}
 R_{2}
 R_{3}
 R_{4}
 R_{4}
 R_{4}

60. A rocaglamide derivative prepared by the method of claim 38, wherein the rocaglamide derivative has the following chemical structure:

61. A rocaglamide derivative prepared by the method of claim 43, wherein the rocaglamide derivative has the following chemical structure:

HO OR'
$$R_{2}$$

$$R_{3}$$

$$R_{4}$$
(VIII).

62. A rocaglamide derivative prepared by the method of claim 44, wherein the rocaglamide derivative has the following chemical structure:

63. A forbaglin derivative prepared by the method of claim 49, wherein the forbaglin derivative has the following chemical structure:

$$R_2$$
 R_3
 R_4
 R_4
 R_8
 R_8
 R_8
 R_8
 R_8
 R_8
 R_8
 R_8
 R_8

64. A forbaglin derivative prepared by the method of claim 50, wherein the forbaglin derivative has the following chemical structure:

$$R_{2}$$
 R_{3}
 R_{4}
 R_{5}
 R_{6}
 R_{7}
 R_{6}

- Use of an aglain derivative (VI) of claim 57 for the manufacture of a medicament.
- Use of an aglain derivative (VI') of claim 58 for the manufacture of a medicament.

Use of a rocaglamide derivative (VII) of claim 59 for the manufacture of a medicament.

- 68. Use of a rocaglamide derivative (VII') of claim 60 for the manufacture of a medicament.
- 69. Use of a rocaglamide derivative (VIII) of claim 61 for the manufacture of a medicament.
- 70. Use of a rocaglamide derivative (VIII') of claim 62 for the manufacture of a medicament.
- 71. Use of a forbaglin derivative (IX) of claim 63 for the manufacture of a medicament.
- 72. Use of a forbaglin derivative (IX') of claim 64 for the manufacture of a medicament.:
- 73. The use as in any one of claims 65-72, characterized in that a medicament for use in the treatment of cancer or a cancerous condition is prepared
- 74. The use as in claim 73, wherein the cancer or cancerous condition is selected from the group consisting of leukemia, sarcoma, breast, colon, bladder, pancreatic, endometrial, head and neck, mesothelioma, myeloma, oesophagal/oral, testicular, thyroid, cervical, bone, renal, uterine, prostate, brain, lung, ovarian, skin, liver, bowel and stomach cancers, tumors and melanomas.
- 75. The use as in any one of claims 65-72, characterized in that a medicament for use in the treatment of a condition associated with cellular proliferation is prepared.
- 76. The use as in claim 75, wherein the condition associated with cellular proliferation is selected from the group consisting of atherosclerosis, restinosis, rheumatoid arthritis, osteoarthritis, inflammatory arthritis, psoriasis, periodontal disease and virally induced cellular hyperproliferation.

77. The use as in any one of claims 65-72, characterized in that a medicament for use in the treatment of a NF-kB-dependent condition is prepared.

78. The use as in claim 77, wherein the NF-κB-dependent condition is selected from the group consisting of inflammatory diseases, immunological disorders, septic shock, transplant rejection, radiation damage reperfusion injuries after ischemia, stroke, cerebral trauma, thromboses, cirrhosis of the liver, asthma, complex, chronic inflammatory disorders, arteriosclerosis, and multiple sclerosis.